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The study on the properties of black multicrystalline silicon solar cell varying with the diffusion temperature

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Abstract

The black multi-crystalline silicon (mc-Si) has been successfully produced by plasma immersion ion implantation. The microstructure and the reflectance of the black mc-Si have been investigated by atomic force microscope and spectrophotometer, respectively. Results show that the black mc-Si exhibits a hillock structure with a low reflectance. Besides, with decreasing the diffusion temperature, the external quantum efficiency of the black mc-Si solar cell increases below ~550 nm wavelength due to reduced surface recombination. The optimal conversion effieciency of the black mc-Si solar cell is 15.50% at the diffusion temperature of 825 °C. Furthermore, it is interesting to find that there are something different between black mc-Si and acid etched mc-Si on the impact of diffusion.

***Keywords*:** black silicon; diffusion temperature; multicrystalline silicon solar cell.

1. Introduction

Reducing surface reflectance to enhance light absorption is very important to improve the conversion efficiency of crystalline silicon solar cell. There can be as high as 30% weighted average reflectance on the surface of original crystalline silicon wafer [1]. Generally, depositing anti-reflection coating (ARC) (for example, SiN_x [2]) is very effective to reduce surface reflectance, but surface texturing is a more permanent and effective solution to eliminate reflections. Anisotropic etching of monocrystalline silicon in alkaline solution is effective to reduce surface reflectance and widely used in industry [3]. But it doesn't work for multi-crystalline silicon (mc-Si) wafer due to randomly orientated crystallites. Instead,

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isotropic etching in acid solution is widely used in industry [4]. The reflectance of acid etched mc-Si is still as high as 25%, leading to a big light reflectance loss.

To further reduce surface reflectance of mc-Si solar cell, various texturing methods have been tried and investigated. J S Yoo et al. [5] have focused on the texturing of the silicon surface by reactive ion etching using a multi-hollow cathode system. The etched mc-Si surface shows almost zero reflectance in the visible region as well as in near-IR region. The low surface reflectance of mc-Si can also be realized by mechanical surface texturization with V-grooved between the front grids [6]. R Torres et al. [7] have successfully prepared black mc-Si wafer with a reflectivity down to 3% by femtosecond laser pulses. The black mc-Si has been investigated by local metal-catalyzed wet chemical etching [8], which results in a very low reflectivity.

Since the surface morphology of the black silicon is different from that of acid etched silicon, the impact of diffusion temperature on black silicon solar cell deserves to investigate. In the present study, the black mc-Si has been fabricated by plasma immersion ion implantation. The influence of diffusion temperature on the properties of the black mc-Si solar cell will be investigated in detail.

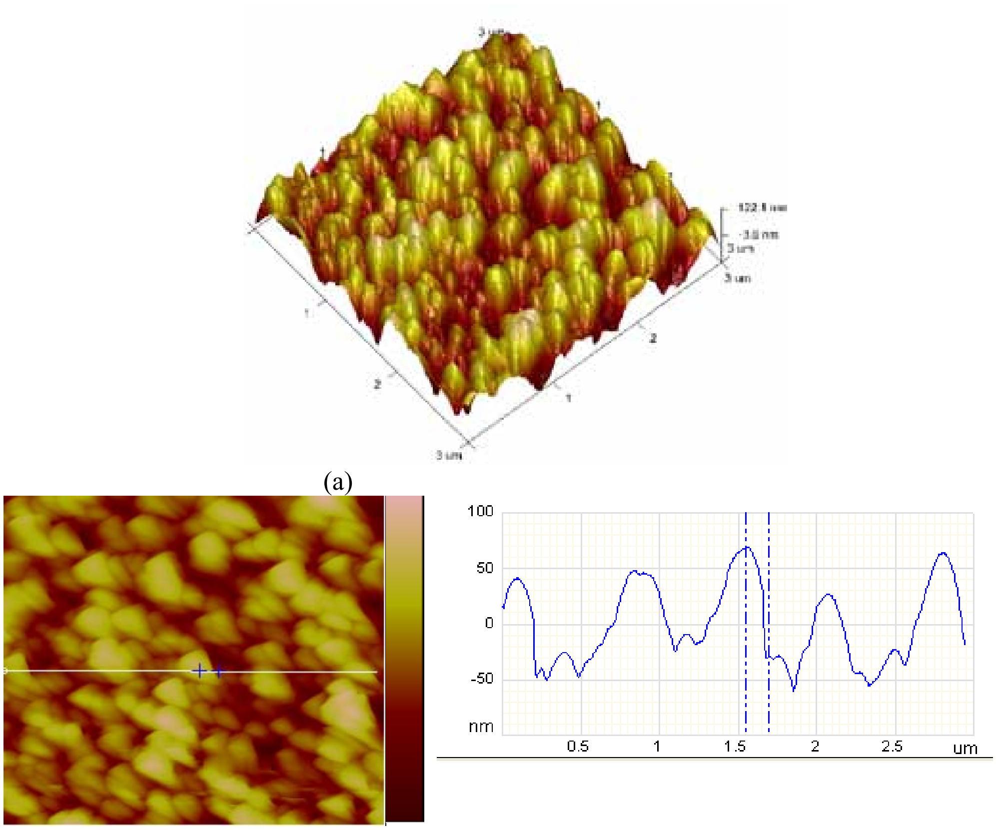
2. Experimental

The material used for experiments was commercially available boron doped p-type multi-crystalline silicon wafers obtained from the ingot by wire sawing of thickness 200 ± 20 μm , area 156 mm × 156 mm and resistivity 1～3 Ω cm. The damage on the surface induced by wire-cutting was removed by etching in 10% NaOH solution at 80 °C. After that the black mc-Si was fabricated by plasma immersion ion implantation process. Sulfur hexafluoride (SF_6) and Oxygen (O_2) gas was bled into the vacuum chamber at a flow rate of 150 and 40 sccm, respectively. 900 W radio frequency power and 500 V negative voltage pulses were applied to the sample stage during the plasma immersion ion implantation process. Then the black mc-Si wafers were subjected to acid etching in 2% HCl and then in 10% HF to remove the contamination and oxides. As a comparison, the reference cells were textured in acid solution contained HNO_3 and HF. The black mc-Si solar cells and reference solar cells (acid etched) were prepared using the same processing. Both the black mc-Si wafers and the acid etched wafers were divided into 5 groups which were phosphorus doped using phosphorous oxychloride ($POCl_3$) as the dopant source at the temperature of 835 °C, 830 °C, 825 °C, 820 °C and 815 °C, respectively. Afterward all the wafers were subjected to edge etching and the removal of phosphosilicate glass (PSG) layer from the diffused wafers surface with diluted HF (10% by volume). Silicon-nitride layer for passivation was grown by plasma enhanced chemical vapor deposition (PECVD) process. Finally, the front and back metallization of all the wafers were carried out by screen-printing technique and followed by baking and co-firing in a conveyer belt furnace.

The microstructure of the black mc-Si has been investigated by atomic force microscope (AFM). The surface reflectance was examined by a UV-VIS-NIR spectrophotometer equipped with an integrating sphere detector. The sheet resistance and external quantum efficiency (EQE) were measured on Four-probe sheet resistance measurement and Solar Cell Scan 100 quantum efficiency measurement system, respectively. The Illuminated solar cell performance was determined by the JR-1250 Solar Cell I. V. Tester and Sorter under one sun global solar spectrum of Air Mass (AM) 1.5 at 25 °C.

3. Results and discussion

Fig. 1 shows the atomic force microscope (AFM) of the microstructure of the black multi-crystalline silicon. It can be seen that the silicon surface is covered with a lot of random hillocks with a diameter ranging from Tens of nanometers to a few hundred nanometers and a height of about 100 nm. This microstructure is the result of the competition between SF^{+}_{x} ($x \leq 5$) and F^{+} ions etching effect and $Si_xO_yF_z$ mask effect [9]. Fig. 1(c) shows the height distribution of the surface along the line which shown in Fig. 1(b). It indicates that the texture is uniform and the lateral sizes of the texture features are smaller than the wavelength of the incident light in the whole range of strong absorption, which will result in a low reflectance.



(a)

(b) (c)

Fig. 1. AFM of the microstructure of the black mc-Si. (a) three dimension image of the structure. (b) two dimension image of the structure. (c) the height distribution of the surface along the line which shown in (b). The height of the hillock is around 100 nm.

Fig. 2 shows a typical normal incidence spectral reflectance of the black mc-Si surface. The reflectance of the acid etched mc-Si is also plotted for comparison. The surface of the black mc-Si shows very low reflectance in the visible as well as in the near-IR regions. The decreased reflectance of the black mc-Si results from the unique structure. For microscopically rough surfaces, both the mean value of irregularity and the corresponding correlation lengths are smaller than the wavelength of the incident light. As a result, the light interacts with the whole surface rather than each rough spot [10]. Moreover, the nanohillock layer is equal to the gradient-index multilayer structure, meaning that the index of refraction changes gradually from air to silicon substrate [11]. As it is known, this is an effective antireflection structure.

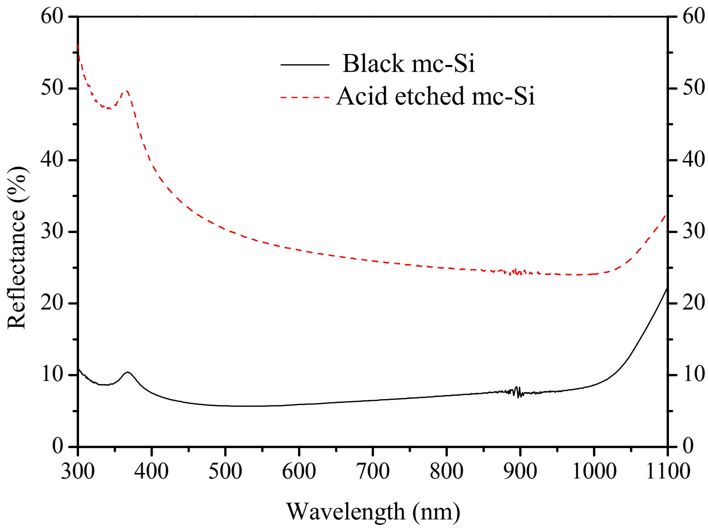


Fig. 2. The reflectance of the black mc-Si wafer and acid etched mc-Si wafer.

The sheet resistance of both black mc-Si and acid etched mc-Si after P-diffusion was measured. Fig. 3 shows the sheet resistance as a function of diffusion temperature from 835 °C to 815 °C. As the diffusion temperature decreases, the sheet resistance of the black mc-Si increases. The reason for this is obvious. In addition, it is interesting to find that the sheet resistances of the black mc-Si are lower than that of the acid etched mc-Si, indicating that the black mc-Si has higher doping concentration under the same diffusion temperature. This is mainly the result of the different microstructures between black mc-Si and acid etched mc-Si. Generally, the black mc-Si wafer has numerous internal surfaces, and this will contribute to easier P diffusion and leading to lower sheet resistance.

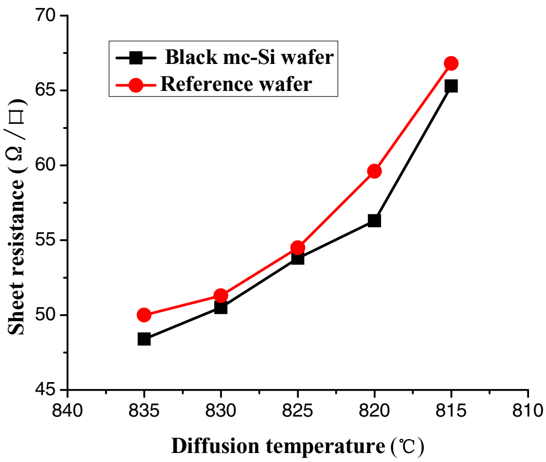


Fig. 3. The sheet resistance of the black mc-Si wafer and reference wafer varying with diffusion temperature.

Fig. 4 shows the EQE of the black mc-Si solar cells with the diffusion temperatures of 830 °C，825 °C and 815 °C, respectively. With decreasing the diffusion temperature, the EQE of the black mc-Si solar cell increase below ~550 nm wavelength. As it is known, higher diffusion temperature leads to higher diffusion coefficient, which will results in higher doping level with the same diffusion time. And Auger recombination is related to the doping concentration. Therefore, higher diffusion temperature results in higher Auger recombination which will worsen EQE in short wavelength.

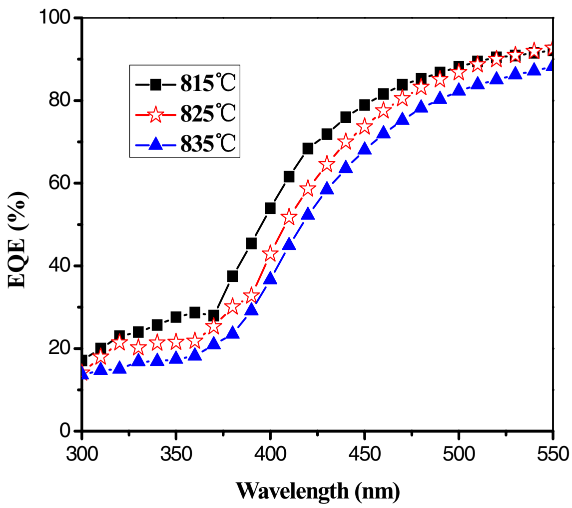


Fig. 4. The EQE of the black mc-Si solar cells with different diffusion temperatures.

Table 1 lists the performance of the black mc-Si solar cells with varying the diffusion temperature. The short circuit current increases while the shunt resistance decreases with decreasing the diffusion temperature. As discussed above, the lower diffusion temperature means the lower doping concentration and lower Auger recombination, which will improve the blue spectral response and lead to higher short circuit current. The influence of the diffusion temperature on the shunt resistance is related to the diffusion mechanism:

$$D = D_{\infty} \exp\left(-\frac{E_a}{kT}\right),$$

Where D is the impurity diffusion coefficient, D_{∞} means impurity diffusion coefficient with infinite temperature, E_a means activation energy, k is the Boltzmann constant and T is the diffusion temperature. It clearly indicates that the lower diffusion temperature, the lower diffusion coefficient, the shallower the depth of the p-n junction. Therefore, in the firing process, the metal particles in silver paste are easier to diffuse into p-n junction which will cause shunt current.

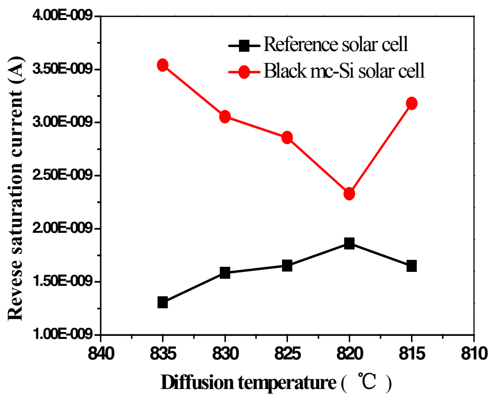
The I-V characteristic of a solar cell can be described as exponential model, defined as follows:

$$I = I_{ph} - I_0\left[\exp\left(\frac{V + IR_s}{nV_t}\right) - 1\right] - \frac{V + IR_s}{R_{sh}}$$

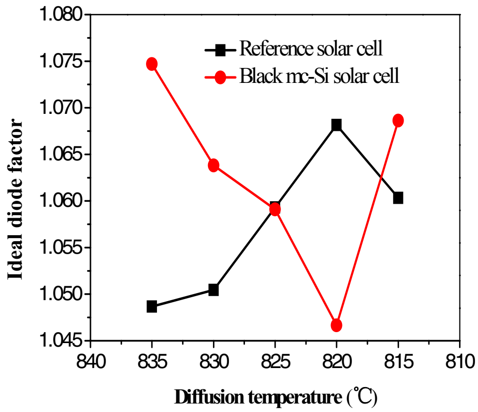
Where V_t is equal to kT/q (k,T and q have their usual meaning), I_{ph} is the photocurrent, I_0 and n meaning the reverse saturation current and ideal diode factor, respectively. The reverse saturation current and ideal diode factor can be numerically solved from this model. Fig. 5 exhibits the I_0 and n varying with the diffusion temperature. It can be seen that the I_0 and n of the black mc-Si solar cell decreases varying with decreasing diffusion temperature, meaning that the recombination current diminished. However, they increase as the diffusion temperature lower than 820 °C. In addition, it is queer to find that I_0 and n of the black mc-Si solar cell change opposite to that of reference solar cell when decreasing the diffusion temperature. This may be attributed to the different surface microstructure between the black mc-Si and the reference solar cell.

Table 1
The performance of the black mc-Si solar cells with different diffusion temperatures.

Temperature(°C)	V_{oc} (V)	I_{sc} (A)	R_s (mΩ)	R_{sh} (Ω)	FF (%)	N_{Cell} (%)
835	0.602	7.962	3.370	121.937	77.720	15.32
830	0.601	8.028	3.256	90.637	77.858	15.45
825	0.600	8.073	3.258	64.804	77.865	15.50
820	0.601	8.082	4.132	62.307	76.766	15.34
815	0.602	8.100	4.355	41.737	76.259	15.31



(a)



(b)

Fig. 5. (a) The reverse saturation current of the black mc-Si solar cells and reference solar cells varying with diffusion temperature. (b) The ideal diode factor of the black mc-Si solar cells and reference solar cells varying with diffusion temperature.

4. Conclusion

The black multi-crystalline silicon has been successfully produced by plasma immersion ion implantation. The black mc-Si surface exhibits hillocks structure with a diameter ranging from tens of nanometers to a few hundred nanometers and a height of about 100 nm. The unique microstructure causes a low reflectance of the black mc-Si. With decreasing the diffusion temperature, the EQE of the black mc-Si solar cell increase below ~550 nm wavelength and the short circuit current can be enhanced. Furthermore, it is interesting to find that the reverse saturation current and ideal diode factor of black mc-Si solar cell have different change compared with that of reference solar cell when decreasing the diffusion temperature.

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